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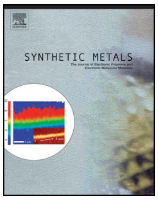

Synthesis and fluorescence properties of a soluble polypyrrole derivative based on a dipyrrole monomer

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ABSTRACT

A unique dipyrrole monomer 2-methyl-1,3-di(1H-pyrrol-1-yl)propan-1-one (MDPP) was synthesized and the corresponding branched polymer (PMDPP) with the molecular weight (M_w) of 2416 was obtained by the chemical polymerization. The molecular structures of MDPP and PMDPP were characterized by FTIR and NMR. It was found that the polymerization of MDPP was accomplished on the pyrrole ring which is attached to the carbonyl group. The resulting polymer had an amorphous structure and could be dissolved in many organic solvents. The fluorescence measurements were carried out on PMDPP solutions, which emitted the green light in the range of 556–574 nm under the excitation of 467 nm depending on the solvents. It is interesting that the Stokes shift of the PMDPP solution was more sensitive to the electron donor–acceptor properties of solvent rather than the polarity of solvent. Notably, the maximum emission wavelength (λ_{max}^{em}) of the PMDPP solution showed a red shift from 556 nm to 586 nm with the increase of PMDPP concentration from $1.80 \times E-5$ g/ml to $6.314 \times E-4$ g/ml in THF, and it exhibited a remarkable dependence on the excitation wavelength in the range of 327–507 nm, which led to a gradual red shift of the λ_{max}^{em} from 510 nm to 584 nm.

1. Introduction

Conducting polymers have been a subject of great interest over the past few decades because of their attractive physical properties, such as light weight, metallic conductivity, rapid non-linear optical responses, reversible convertibility between redox states and excellent electrochromism [1–3]. Based on these properties, conducting polymers have been widely investigated for applications in photovoltaic cell, electrochromic device, field emission displays, surface protection, chemical and biological sensors and actuators [4–6].

Among several types of conducting polymer, polypyrrole stands out to be the focus of research because of its significant environmental stability, excellent biocompatibility, highelectrical conductivity and relative ease of synthesis [7–9]. However, polypyrrole exhibits poor solubility due to the strong intermolecular and intramolecular interactions, limiting its potential applications in many areas greatly.

Up to now, diverse synthetic strategies have been developed to improve the processability of polypyrrole. These methods include: (1) preparation of composites of polypyrrole by physical mixing or in situ polymerization [10,11]. It indicates that the composites obtained in this way always possess both the excellent processability and the controllable conductivity. (2) Synthesis of soluble polypyrrole in the presence of functional dopants or surfactants with the large counter-anions, such as dodecylbenzenesulfonic acid and amphiphilic azobenzenesulfonic acid [12,13]. The counter-anion with a large size can reduce the intermolecular and intramolecular interactions of polymer chains and then improve the solubility of polypyrrole [14]. (3) Preparation of polypyrrole-based copolymer with conventional polymer by the chemical or electrochemical polymerization [15]. The properties of the copolymer can be adjusted by varying the nature or the ratio of the polymer copolymerized with polypyrrole [16]. (4) Synthesis of soluble polypyrrole derivatives through the modification of the pyrrole monomer. Many investigations have been carried out on

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Abbreviations: MDPP, 2-methyl-1,3-di(1H-pyrrol-1-yl)propan-1-one; PMDPP, the polymer of 2-methyl-1,3-di(1H-pyrrol-1-yl)propan-1-one.

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this method because of the ease of polymerization and the broad selectivity of substituents that can be introduced to pyrrole ring [17–19]. The resulting polymer would have the unique functions depending on the introduced substituent [20].

Among the numerous investigations about the preparation, property and the application of polypyrrole derivatives [21,22], there are several reports focused on N-substituted dipyrrole monomers and corresponding polymers [23–25]. It is worth noting that most of the reported dipyrrole monomers had the regular structure, with two N-substituted pyrrole rings linked with the symmetrical spacer. However, the polymers of these monomers were always insoluble because both pyrrolyl moieties of the monomer were involved in the polymerization, forming ladder-like or network polymers [23,24]. The preparation of soluble polypyrrole derivative based on the dipyrrole monomer has rarely been reported.

In this paper, a N-substituted dipyrrolyl monomer 2-methyl-1,3-di(1H-pyrrol-1-yl)propan-1-one (MDPP) was synthesized, and its soluble polymer (PMDPP) was prepared by the chemical polymerization. The effects of two N-substituents to the polymerization of each pyrrole ring in MDPP were analyzed. Additionally, the properties of PMDPP were presented, especially fluorescent properties.

2. Experimental

2.1. Materials

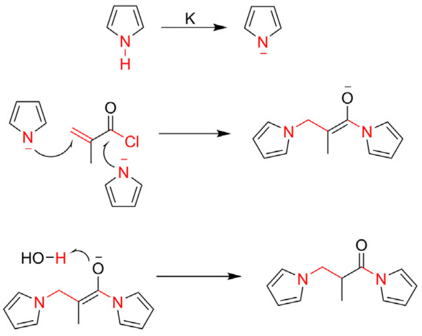
Pyrrole (99.5%, Zhejiang Taizhou Qingquan Medical & Chemical Co., Ltd.) was vacuum-distilled and stored in the absence of light before use. Methacryloyl chloride was synthesized according to a previously reported method [26]. Potassium (K, analytical grade, 99%), iron (III) chloride ($FeCl_3{\cdot}6H_2O$, analytical grade), lithium perchlorate ($LiClO_4$, analytical grade) and analytical grade solvents of acetonitrile, dichloromethane (DCM), tetrahydrofuran (THF), isopropanol (IPA), chloroform (CLF), acetone (ACT), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

2.2. Synthesis of MDPP

A small piece of potassium (0.05 mol) was added to 30 ml dry THF in a round bottom flask, under the protection of nitrogen. Then, freshly distilled pyrrole (0.05 mol) was added at once. The mixture was stirred magnetically at room temperature (28 ± 2 °C) until all the potassium was consumed. Subsequently, 20 ml THF solution of distilled methacryloyl chloride (0.025 mol) was added dropwise using a dropping funnel. After 24 h, the precipitate was filtered and the solvent THF was distilled off from the filtrate. The crude product was washed with a saturated aqueous solution of sodium sulfate for several times. After separation and drying, the product was further purified by silica gel column chromatography using DCM as the eluent. The monomer MDPP was obtained in a yield of 79%. ^{1}H NMR: (400-MHz; DMSO-d6, ppm) 7.47 (s, 2H), 6.75 (s, 2H), 6.31 (s, 2H), 5.94 (s, 2H), 4.26 (m, 1H), 4.02 (m, 1H), 3.85 (m, 1H), 1.14 (d, 3H); ^{13}C NMR: (100 MHz; $CDCl_3$, ppm) 172.18, 120.96, 118.94, 113.61, 108.65, 51.90, 41.27, 16.40.

2.3. Preparation of PMDPP

The monomer MDPP (0.002 mol) was added to 80 ml deionized water with stirring in a nitrogen atmosphere. Then 20 ml aqueous solution of $FeCl_3$ (0.005 mol) was added dropwise into the above mixture. After a few minutes, the color of mixture turned gradually from orange to black. The polymerization continued for 24 h at room temperature (28 ± 2 °C). When the reaction was terminated, the suspended particulates were filtered and washed with deionized water for several times. After drying in vacuum at 50 °C for 24 h, PMDPP was obtained.



Scheme 1. Synthesis of MDPP.

2.4. Characterization

The chemical structures of MDPP and PMDPP were confirmed by FTIR spectra on a Nicollet AVATAR-IR 360 spectrometer and NMR spectra on a Bruker (Advance III) 400 M Hz spectrometer. Gel permeation chromatography (GPC) measurement of PMDPP was carried out in THF on a Waters-Breeze instrument. The morphologies of PMDPP powders and the spin-coated films were observed in VE-9800S and JSM 7000F scanning electron microscopes, respectively. XRD analysis of PMDPP powders was performed using a Shimadzu XRD-6000 instrument with a Cu Kα X-ray source. Electrical conductivity measurements were performed using a standard four-probe apparatus (SX1944 digital instrument). UV–vis absorption spectra of PMDPP solutions were recorded with a UV-2550 spectrophotometer. Fluorescence of PMDPP solutions was obtained on a fluorescence spectrometer (F900, Edinburgh Instruments). The cyclic voltammogram was performed on ITO-coated glass electrode in acetonitrile solution with a potential range from −0.1 V to 1.5 V at 100 mV/s. The solution contained 0.1 M $LiClO_4$ as the supporting electrolyte together with 0.01 M monomer MDPP. A platinum sheet was used as the counter electrode, and the saturated calomel electrode (SCE) was used as the reference electrode.

3. Results and discussion

3.1. Synthesis and characterization of MDPP

MDPP was synthesized according to the procedures shown in Scheme 1. The redox reaction of pyrrole and potassium led to the formation of pyrrole anion, which is very reactive. Subsequently, two types of reaction may occur between pyrrole anion and methacryloyl chloride. On the one hand the pyrrole anion undergo the nucleophilic substitution reaction with acyl chloride group of methacryloyl chloride [27]. On the other hand pyrrole anion undergo the Michael addition reaction with C═C group of methacryloyl chloride [28–30]. The experimental conditions of the synthesis of MDPP were pre-explored. It was found that the product was sensitive to the reaction temperature. When the reaction was carried out in an ice-water bath, the second addition reaction could be suppressed, and then N-methacryloyl pyrrole was obtained. It was consistent with the previous report [27]. However, When the reaction was carried out at room temperature (28 ± 2 °C), the Michael addition reaction occurred simultaneously. Then, two pyrrole rings were linked by a spacer, forming the monomer MDPP. The FTIR spectrum of the product (Fig. 1a) shows the characteristic bands of pyrrole ring at 1547 cm^{-1} and 1467 cm^{-1}, while the band at about 3400 cm^{-1} due to the N—H bond of pyrrole monomer is